



Mechanisms of dendritic growth investigated by *in situ* light microscopy during electrodeposition and dissolution of lithium

Jens Steiger^a, Dominik Kramer^{b,*}, Reiner Mönig^{a,b}

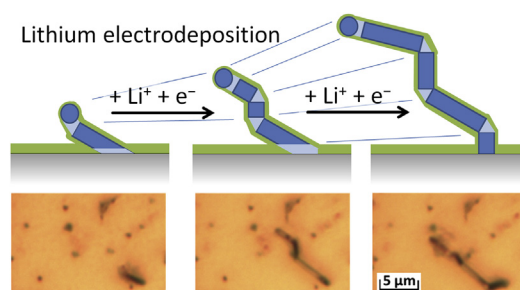
^a Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

^b Helmholtz Institute Ulm (HIU) Electrochemical Energy Storage, Albert-Einstein-Allee 11, 89081 Ulm, Germany

HIGHLIGHTS

- We obtain *in situ* videos at the optical resolution limit in a commercial electrolyte.
- Li needles can grow simultaneously at the substrate–Li interface, at kinks or tips.
- Dissolution thins lithium needles; a SEI shell remains; tips stay inactive.
- The observations are not compatible with known mechanisms of dendritic growth.
- A new mechanism of insertion at defects is suggested.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 26 November 2013

Received in revised form

3 March 2014

Accepted 7 March 2014

Available online 21 March 2014

Keywords:

Lithium metal

Battery

Electrodeposition

Dendritic growth

Growth mechanism

Optical images

ABSTRACT

Batteries with metallic lithium anodes offer improved volumetric and gravimetric energy densities; therefore, future batteries including the promising lithium–sulfur and lithium–air systems would benefit from them. The electrodeposition of lithium metal – which is an unwanted incident in lithium ion systems – often results in fine filaments or moss, called dendritic lithium, which leads to strong capacity fading and the danger of internal short circuiting. To study the mechanisms of dendritic growth and the behavior during lithium dissolution, lithium deposits have been observed *in situ* in 1 M LiPF₆ in EC:DMC by light microscopy. The high resolution optical microscopy provided information on the growth and electrodisolution of single lithium filaments. The growth areas could be identified in detail: The lithium wires can grow either from the substrate–lithium interface, at kinks or in a region at or close to the tip. Based on these observations, we suggest a growth model for lithium filaments predicated on defect-based insertion of lithium at the aforementioned locations. This type of growth is not compatible with previous models of dendritic growth, for example, it is hardly influenced by electric fields at the tip and does not depend on the direction of the electric field.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Lithium-ion secondary batteries are the state of the art technology for portable electric energy storage. They have taken a

leading role in the power supply of mobile electronics and of electric cars. This is due to their high energy and power densities. Lithium-ion batteries usually use graphitic anodes and intercalation materials as cathodes [1].

The use of pure lithium metal instead of graphite strongly improves the volumetric and specific energy density of cells. Lithium metal electrodes have the lowest electrochemical potential and a superior specific capacity; they are required to take full advantage

* Corresponding author. Tel.: +49 721 608 248 94; fax: +49 731 503 4009.

E-mail address: dominik.kramer@kit.edu (D. Kramer).

of possible future technologies such as Li–S or Li–O₂ cells. While pure lithium metal anodes are common in primary batteries, the so-called lithium dendrite growth during charge is the main inhibitor of the usage of those anodes in secondary batteries. Even though today's lithium-ion batteries do not contain metallic lithium, they can still suffer from dendrite growth for high rates of charging especially at low temperatures.

The term “dendrite” is used in different areas of technology and science, such as metallurgy and mineralogy, to refer to a branched, tree-like structure which for example can be formed by solidification from a liquid phase. During electrodeposition of metals, dendritic growth is very common and the issue of dendritic growth during battery charging has been discussed in detail already decades ago, e.g. in Ref. [2]. For the case of lithium plating though, dendritic deposition occurs at comparatively low currents [3].

The phenomenon of dendritic growth of lithium is known since the 1960s [4] or early 1970s [5] but so far only limited understanding of this process exists. Several models and explanations have been proposed and some will be presented in the following, but as of now no general agreement on the basic growth mechanism is reached.

Cohen et al. [6] proposed a model that focuses on the complicated nature of solid-electrolyte interphase (SEI) formation. They argue that in a non-aqueous solution, the SEI – “being a mosaic-type, multilayered structure, due to the large variety of possible surface reactions” – is intrinsically non-uniform in the nanometer and even in the micrometer scale. This causes localized deposition and dissolution at parts of the SEI that have a higher ion-conductivity due to their smaller thickness or more ion-conductive composition. This causes stress between the shape changing lithium layer and the SEI on top. For high current densities, the SEI might not be able to withstand the induced stress and cracks, which reveals an area of the lithium without SEI, which will increase the localization even further. During dissolution, the inhomogeneous current distribution causes deep pits in the lithium, and for plating this can be the cause for dendritic growth.

Another important factor can be the ionic concentration gradient in the electrolyte. During deposition, the concentration of metal cations will drop at the negative electrode where these ions are removed from the electrolyte, while their concentration will rise above the initial value close to the positive electrode where metal cations enter the electrolyte. For high charge rates and especially in dilute solutions the metal cation concentration can drop to zero so that the electrode process switches from a charge transfer to a mass transfer controlled process. This is described by the Sand's behavior, and the Sand's time gives the time needed for the ionic concentration to drop to zero [7]. Despić and Popov [8] identified the influence of a complete concentration polarization on the ramification of the electroplated species. On this basis, Fleury et al. [9] and Chazalviel [10] established their own mathematical growth model and found that once the ionic concentration has dropped to zero, the condition of electro-neutrality in the electrolyte is violated at the negative electrode. This supposedly leads to a local space charge, and ramified structures are expected to form. These structures are predicted to grow at the speed of the anion drift velocity in the electrolyte, and they are expected to form after Sand's time has passed. Brissot et al. [11] experimentally confirmed ramified structure growth at anion drift velocity in a lithium/PEO–LiTFSI/lithium cell and Rosso et al. [12] found that ramified growth of lithium starts at Sand's time even at conditions when Sand's behavior is not expected.

Barton and Bockris [13] proposed a model for dendrite growth below the limiting current based on the fact that deposition from a liquid electrolyte will be faster on thinner and elevated parts of the

surface as they will benefit from a spherical diffusion flux. While on ideally flat surfaces linear diffusion conditions will dominate, a 3D diffusion will be dominant for protrusions. For a spherical diffusion flux, the highest current densities and fastest growth occur at the dendrite tips with the smallest radius. Since experimental results report a round or flat tip with a rather constant diameter of the dendrite, they introduced the surface energy to counteract the tendency of thinning of the dendrite tips and to limit the growth rate. Monroe and Newman [14] and Akolkar [15] expanded the model of Barton and Bockris to allow for changing ionic concentration in the electrolyte. Monroe and Newman's model predicts that a dendrite accelerates with time and passed distance. It is also predicted to grow faster for higher current densities, and can be slowed down by reducing the current during the plating process.

It is also a well-known electrostatic effect that the charge carriers in an electrically polarized volume will not distribute evenly across the volume, but will show a higher charge density close to the surface of the volume. The charge density will become even higher in and at protrusions. This can lead to a stronger electric field there. It has been argued that this is also the case for protrusions on a charged electrode surface inside an electrochemical cell, and it has been suggested that this locally enhanced electric field causes dendrite growth by preferred deposition at the tip of the protrusions [16,17]. This effect might be self-enhancing, as deposition at the tip of a protrusion further increases its length, and hence increasing the local electric field.

A theory that sees dendritic growth as whisker growth was put forward by Yamaki et al. [18]. They believe that lithium that gets plated non-uniformly underneath the SEI creates a stress between the SEI and the underlying lithium substrate. This stress eventually causes the SEI to crack, and the rather soft lithium gets extruded through the crack to relief the stress. This implies that for growth in the whisker-like regime the dendrite grows from the base, and not from the tip like stated in the other models. Once the electrode surface is densely covered by dendrites, ionic transport to the surface is hindered, and lithium gets plated at the whiskers, preferably at dendrite kinks or tips [18].

The different theories describing dendritic growth that have been developed are not compatible with the experimental results: Models based on the ionic transport in solution (spherical vs. planar diffusion, concentration gradient, edge effect) assume that a dendrite grows at its tip; in the diffusion limited aggregation models, [19] the attachment occurs at the existing structures. The observations of Yamaki et al. [18] and Crowther and West [20] clearly demonstrate that the growth does not always occur by attachment to external parts, e.g. the tip. However, their observations are based on dendritic bushes and not on single needles which can grow by different mechanisms. Yamaki et al. [18] proposed the only model describing the growth from the base for dendritic needles. They assume stresses in the lithium for driving plastic flow and feeding lithium to the growing needle. This model has been criticized by Monroe and Newman [14] for the assumptions on the flow behavior of lithium. Due to these inconsistencies, detailed *in situ* experiments as described here are necessary to elucidate the mechanism(s) of dendritic growth of lithium. Since battery electrolytes are intransparent to the electron beam of an SEM, *in situ* SEM cannot be used to study the growth behavior of dendrites completely immersed in an electrolyte. Therefore, we used a high resolution light microscopy setup and *ex situ* SEM to complement the observations. Our results focus on growth and dissolution of lithium structures and not on their nucleation which depends on the substrate material. Here, we used a tungsten substrate since tungsten does not alloy with lithium.

2. Experimental section

Electrodes were created by sputter depositing tungsten (Leica EM SCD 500, pressure $\leq 10^{-6}$ mbar before sputtering, target: 99.8%) onto a borosilicate glass, using tape lift-off to structure the 10 nm thick films (thickness measured with a Leica QSG100). A vacuum system (Leica EM VCT 100) was used to transfer the glass slides to an argon-filled glove box (H_2O and O_2 content < 0.1 ppm).

The *in situ* cells were assembled inside the glove box. The cell body consisted of a poly-ethylene frame in between a borosilicate cover glass and the glass slide (Fig. 1). On one electrode we placed a piece of lithium metal (99.9% from Alfa Aesar) while the other remained untreated. The cells were filled with a commercial LP30 electrolyte (1 M LiPF_6 in a 1:1 weight ratio mixture of EC and DMC) from Merck. The cells were sealed gas tight and were placed under an Olympus BXFM microscope at ambient conditions. We took light microscopy images in bright field mode with a CCD camera. A potentiostat (COMPACTSTAT.e, Ivium Technologies B.V.) was used to galvanostatically cycle our cells at current densities of $\sim 2 \mu\text{A cm}^{-2}$. The area of the working electrode was measured based on light microscopy images with lower resolution ($10\times$ magnification).

3. Results

Fig. 2 shows a typical galvanostatic voltage vs. time plot of lithium deposition on a tungsten substrate. The initial open circuit voltage was around 1.5 V and started to drop once a negative current was applied. The curve started to change slope between 1 V and 0.5 V and after a slight negative peak, the first plated structures became visible on the substrate. The voltage asymptotically approached a small negative value while deposition. Upon change of the direction of the current, the dissolution was visually observed. During lithium dissolution the voltage remained at a similar absolute value than during deposition but stayed positive. After a while the voltage rose. When reaching 2.5 V, the electrical circuit was opened and during relaxation a potential of 2 V was asymptotically approached.

We observed the growth of needle-like lithium on tungsten substrates via *in situ* light microscopy. The needles either grew directly on the tungsten substrate (Fig. 3) or from larger lithium particles (Fig. 4). During growth, an increase in diameter was not observed, while they significantly gained in length. The needles consisted of several straight linear segments of a few microns in length and kinks between these segments. No preferred growth direction was found, e.g. the needle in Fig. 4 grew almost parallel to the substrate while the needle from Fig. 3 grew away from the substrate.

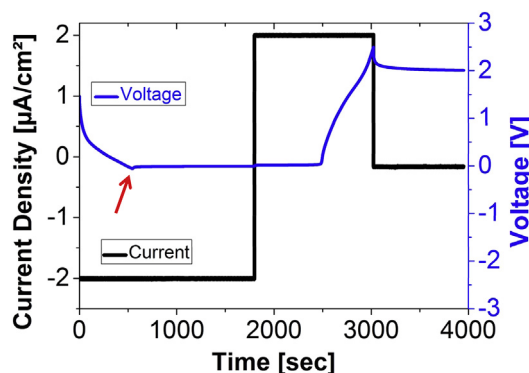


Fig. 2. Galvanostatic voltage vs. time plot of a glass cell with a sputtered tungsten substrate. The red arrow marks a potential peak. The current density is related to the exposed tungsten working electrode area (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

Fig. 3 shows the growth of a needle that grew at the base. The long tip structure of Fig. 3 a) (traced in white) remained unchanged throughout the entire growth of the needle, while the part of the needle that was close to the substrate increased in length. In b) it can be seen that the segment at the base gained in length. In picture c) of Fig. 3, the arrow marks a kink that formed at the base of the needle. In d) the kink had moved forward in the direction of growth. Needles were also observed to grow by adding material to the tip. In Fig. 4 a) another needle that grew from a larger particle is shown (see also Supplementary Video S1 which can be found online at <http://dx.doi.org/10.1016/j.jpowsour.2014.03.029>). It exhibits a kink, marked by an arrow. During its growth, it formed an additional kink as shown in b). Contrary to Fig. 3, the kinks stayed and did not move during further growth as can be seen for example by comparing c) and d). This observation is indicative of tip growth because growth at the base would have caused motion of the kinks as was observed in Fig. 3. Besides growth at the base and growth at the tip also growth can happen between kinks. Fig. 5 shows a filament structure with two pronounced kinks. During lithium deposition, the segment between the kinks elongates. In some cases, the extension between kinks was associated by a change in the kink angles which can be seen by comparing a) with c). We also found lithium filaments that simultaneously grew at several points including base, top and in between kinks. For example, a needle has been observed with three segments that gained in length at the same time. Although these three different growth sites can be clearly identified, from the observations it seems that growth at the base was most common. Growth at the top and in between two kinks was somewhat less common.

According to the voltage vs. time plot (Fig. 2) a significant amount of the plated lithium could be dissolved ($\sim 55\%$). In the case of the dissolution of a lithium filament, the tip was left behind only connected to the substrate by a thin wire-like structure (Fig. 6 and Supplementary Video S2 which can be found online). Both, this tip and the thin connecting remnants could not be dissolved. The dissolution started in the vicinity of the tip, thinning the needle locally. As dissolution progressed, the thinned area moved downwards, similar to the sharpening of a pencil, while the tip itself did not change its position.

4. Discussion

Nishida et al. [21] claimed that the slight voltage peak (see red arrow in Fig. 2) is caused by a reduction of a thin surface oxide layer.

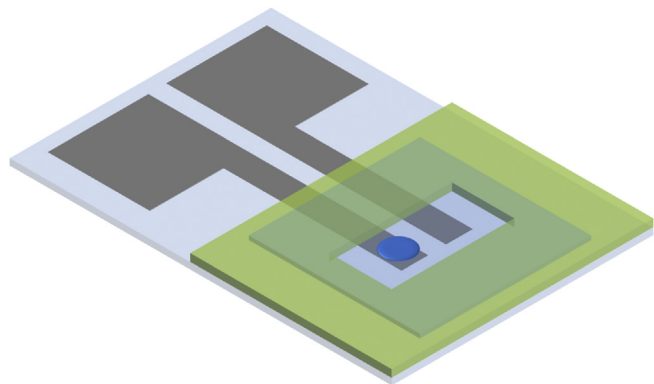


Fig. 1. *In situ* light microscopy cell setup. The tungsten electrodes are drawn in gray, the PE frame in green and Li in blue (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

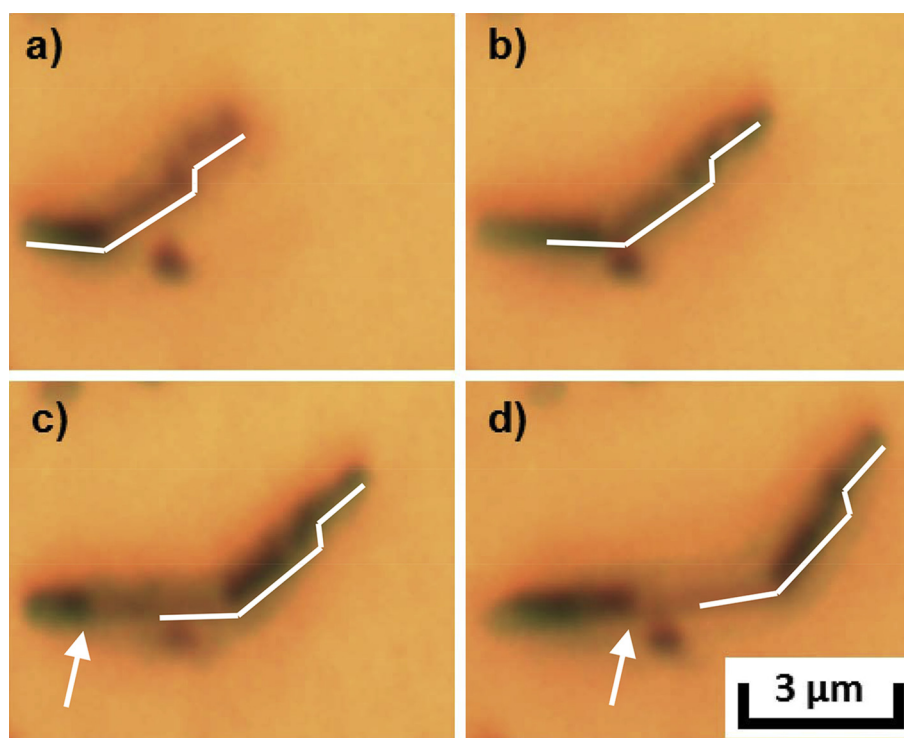


Fig. 3. *In situ* light microscopy of needle-like lithium growth in 1 M LiPF₆ electrolyte. The structure of image a) (traced in white) remains unchanged, while more segments are added at the base of the structure as shown in the subsequent pictures, i.e. the images demonstrate that in this case the growth occurred exclusively at the base of the needle. A kink forms in c) and is marked by an arrow. Image b) was taken after 15 s, c) after 180 s, and d) after 450 s after image a) was recorded.

Sagane et al. [22] attributed this peak to the nucleation and growth process since he observed that first precipitation occurred after the peak. This is also our interpretation, as we have observed this peak reoccurring during deposition following a complete dissolution of the Li. This peak was also absent during plating on Li metal where no nucleation process is expected. The change in slope of the voltage curve below 1 V is interpreted as solvent decomposition and formation of the SEI.

The tip of a dissolving needle appears to be inactive, i.e. there is always distinct structure remaining after the lithium is dissolved. We suggest that the part that is inactive during dissolution might be also inactive during deposition, see Fig. S3; hence, what appeared as deposition on the tip is rather a deposition of lithium between the inactive tip and the active lithium metal of the needle. The fact that lithium needles grew in length, but not in diameter, means that atoms are not attached to the sidewalls of the needle but instead are inserted close to the tip or at the needle–substrate interface. Growth between two kinks additionally suggests lithium insertion at kinks. Adding atoms always at the same location probably leads to the constant diameter of a segment. Our observations indicate that the growth of Li filaments is defect controlled and that lithium atoms are inserted into the crystal at defect sites. This suggests that conventional explanations based on field and concentration gradients are not adequate for the case of our experiments.

During deposition, the SEI forms on the freshly grown lithium while during dissolution, the SEI cannot be removed. This has important consequences when comparing deposition with dissolution. Fig. 6 shows the removal of lithium along the needle and the persistence of the structure at the tip. This suggests that an SEI shell remains that holds the structure at the tip in the same position while the lithium inside this shell dissolves. The thin wire-like – supposedly tubular – structures of Fig. 6e) and f) that remained

after dissolution are possibly these residues of SEI which are visible after the dissolution of the metal only because SEI attached to reflecting metal cannot be resolved by light microscopy. Although the dendrites were growing in length and not in diameter, the dissolution includes a thinning process starting at the tip instead of a pure shortening process. Shortening of the whole structure might be impossible because of the constraints of the SEI shell.

The inactive tips may consist of metal oxides or lithium salt, e.g. LiF, or other impurities which can act as catalysts for lithium insertion. LiF crystals have roughly the size of a dendrite and resemble the shape of inactive needle tips [23]. This may explain why the tip shape of a needle does not change during growth, e.g. in Fig. S3. Using synchrotron hard X-ray microtomography, small crystalline contaminants were found underneath every growing dendrite in a lithium polymer cell also indicating that contaminants may act as catalysts for dendrite growth [24]. In the literature, a flat and even distribution of LiF was observed to prevent dendritic deposition [25]. LiF was used here as an example. The inactive tip could for example also just be a relatively thick SEI layer locally grown on the lithium nucleus probably during onset of metal deposition, i.e. the parts (b)–(f) of the illustration remain valid for a growth without an initial extra structure as shown in (a).

5. Comparison to other models

None of the previously proposed models seem to be able to explain the growth behavior observed here. The model proposed by Cohen et al. [6] offers a conclusive explanation for dendrite growth initiation. The SEI also has been accepted as one of the major influences on dendrite growth [6,23,25]. However, crack formation in the SEI alone cannot explain why needle-like growth was observed instead of the growth of three dimensional bulk structures. On surfaces of freshly grown structures there is also a fresh, i.e. thin

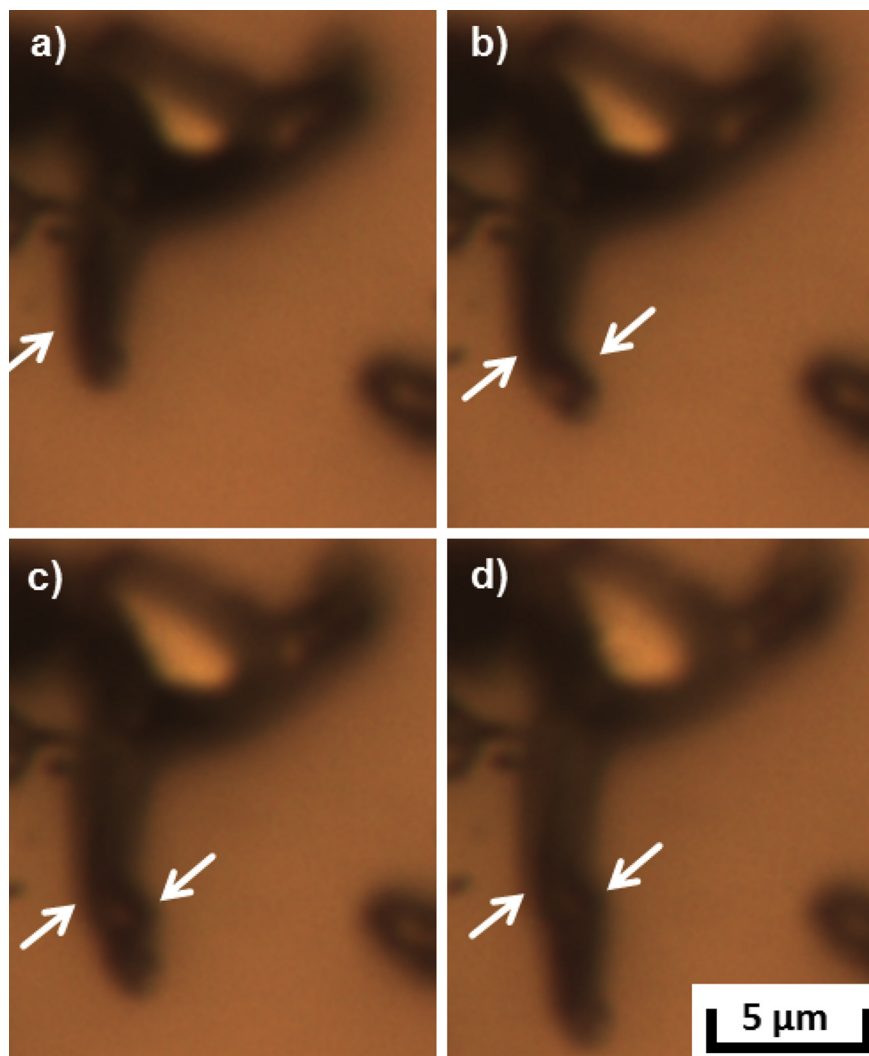


Fig. 4. *In situ* light microscopy of needle-like lithium growth in 1 M LiPF₆. Image a) shows needle-like lithium. The needle forms a kink (marked) in image a) and another kink (marked) in image b). Image c) and d) show that during further growth the size and position of the needle segments and kinks did not change, instead the tip segment of the needle grew in length. Image b) was taken after 105 s, c) after 195 s, and d) after 360 s.

layer of SEI. If the resistivity or thickness of the SEI controls the growth, it can be expected that either growing filaments not only grow in length but also in diameter or that branches nucleate on them more frequently. Furthermore, a deposition at the base of the structures seems unfavorable from the SEI point of view due to the thick SEI layer on the substrate. Defects of the SEI which may be present at kinks would result in a lithium deposition there, as illustrated by the round deposit shown in the supporting Fig. S4b). Lithium deposition at kink sites (shown as circular shapes in the model in Ref. [18]) was described explicitly for a LiAsF₆ electrolyte by Yamaki et al. [18]; we did not observe such a deposition at kink sites for the 1 M LiPF₆ solution.

The models featuring the ionic concentration gradient [9–12,15] predict a preferred growth direction into lithium ion rich areas of the electrolyte which is usually towards the counter electrode. In the case of our cell, the needles should have all grown towards the left in Fig. 1, but instead we observed what looks like a random distribution of growth directions. These models are also limited to deposition at the tip of a structure and hence fail to explain the observed atom insertion at the base. In addition, considering the current densities studied in our work, no significant concentration gradients are expected.

The growth predictions of the edge effect in electric fields [13,14], the spherical diffusion flux [16,17] and diffusion limited aggregation [19] are not limited to preferred growth directions, but are also limited to growth at the tip or at outer contours. In these cases deposition at the base of a needle is unfavorable, in the case of the electric field due to the locally weakened field, in the case of the diffusion flux because diffusion paths to the base are longer and are often obstructed by the already deposited structures. The spherical diffusion flux model by Monroe and Newman [14] additionally predicts that the growth of a needle accelerates with time. For our galvanostatic conditions, we found that needles continually decelerated and eventually seized to grow.

Up to now, the model of Yamaki et al. [18] of whisker-like growth has been the only one to explain the observed growth at the base of a needle. They were also the first ones to introduce the term “whisker” instead of dendrite, which is consistent with what we call needle-like growth. A classical dendrite in materials science or electrochemistry describes a fern- or snowflake-like structure [26] that is growing by deposition at the tip, whereas a classical whisker is typically a crystalline structure, often with a high aspect ratio. The mechanism of growth of many whiskers is still not clear but whiskers are considered to either grow from the tip or base. An

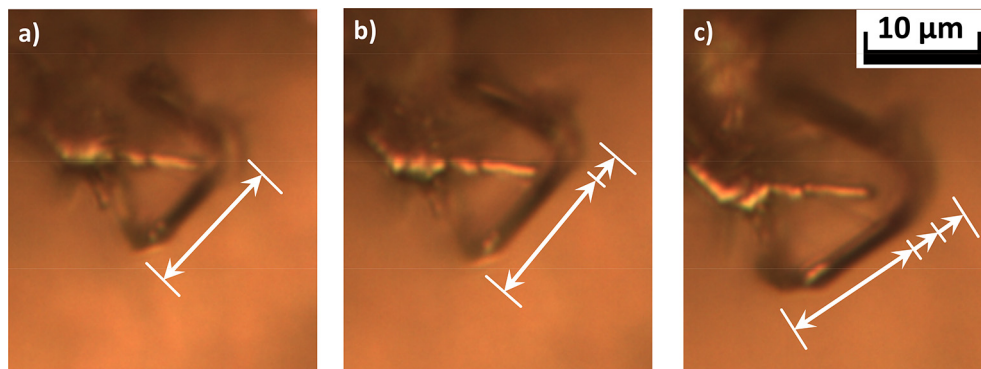


Fig. 5. *In situ* light microscopy of needle-like growth in 1 M LiPF₆ on a lithium substrate. The view on the tip and the base of the needle is obstructed by other lithium structures, three straight segments connected by two kinks can be seen. Images b) and c) show that the segment between the kinks grew in length (marked by white arrow). Image b) was taken after 45 s, and c) after 135 s.

observation like the one made here, where growth happens at the base, at the tip, as well as between two kinks is not in agreement with conventional whisker growth models. The model by Yamaki et al. where lithium whisker growth is described as a stress induced process similar to the growth of tin whiskers, can hardly explain the growth within a kinked filament as shown in Fig. 5, as this would require another extrusion process inside the whisker. This is unlikely due to the following: i) at the growing structure, the SEI should be thin. Therefore, the stress buildup which is supposed to be related to the confinement of the SEI film would be smaller than on the structures deposited earlier. ii) Within the whisker, there is no extrusion hole. iii) There is hardly a pressurized volume and only a limited surface area around kinks to supply enough lithium for this growth mechanism. From the observations performed here, it seems that the formation of lithium whiskers can occur without stresses or – more precisely – stress gradients that trigger the formation of tin whiskers [27]. It can be concluded that the

extrusion model is not suitable to explain the filament growth for the electrolyte and rate used here. We suggest that the growth occurs by immediate addition of lattice planes to the existing whisker.

A consequence of this rather local insertion is that shorter diffusion paths inside the solid are required as compared to tin whisker growth. During whisker growth, diffusion of tin atoms towards the whisker along grain boundaries over distances of several microns occurs. For the mechanism considered here (Fig. 7) the maximum distance is the diameter of the lithium filament. Another important process might be surface diffusion: For tin, lateral diffusion over enormous distances is possible [28]; similar to that, we consider surface diffusion of lithium atoms as a possible mechanism for the delivery of the atoms needed for growth.

The whisker-like growth of the lithium filaments observed here with a growth at the base is quite different from the usual dendritic growth which – by the definition of “dendrite” – includes

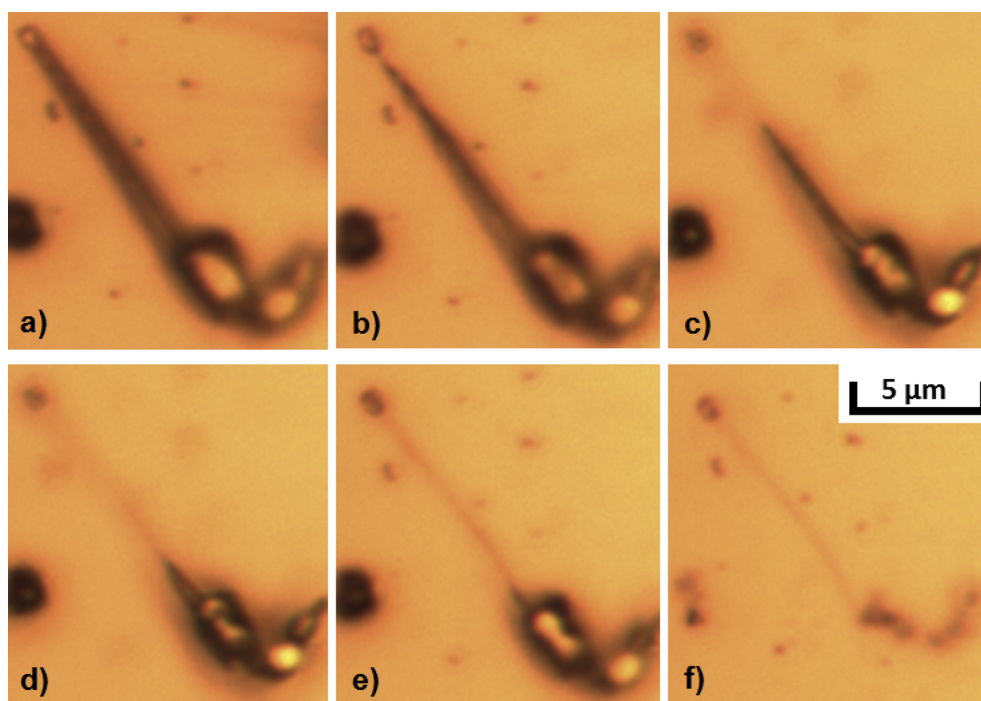


Fig. 6. *In situ* light microscopy of the electro-dissolution of a lithium needle. Image a) shows the initial needle and images b)–f) its dissolution. In image b) the dissolution is a thinning process localized to the area near the tip leaving a tapered needle. As this region is dissolved, the thinning area moves downwards, similar to the sharpening of a pencil. The tip and a thin wire could not be dissolved. Image b) was taken after 240 s, c) after 285 s, d) after 360 s, e) after 390 s, and f) after 585 s.

branching. Typical dendrites often have a regular, quasi-periodic branching pattern, but irregular structures occur for the conditions where the diffusion limited aggregation model [19] applies. No regular branching has been observed by us or reported in the literature for lithium deposits, i.e. the known “lithium dendrites” are irregular, non-uniform structures.

It has already been reported that Li needles can grow at either the tip or the base in a imidazolium chloroaluminate electrolyte, for which needles are expected to be much larger than in conventional electrolytes [29]. In our case, we observed Li filament growth in the widely-spread EC/DMC/LiPF₆ electrolyte, even though dendrites in EC:DMC have been told to be too small to be imaged using a light microscope [29]. Our key observation is that lithium metal filaments do not grow exactly at the tip, but behind an inactive structure at the tip and that growth is also possible in between the base and the tip. Both processes require the insertion of metal atoms. This can happen at the substrate–lithium interface or at crystalline defects such as kinks since the insertion of atoms into the volume of an intact crystalline solid is unlikely from an energetic point of view. It may be possible that the efficiency of the defect for lithium insertion depends on the degree of crystalline disorder associated with the defect. In this context, large angle boundaries or amorphous regions could lead to fast insertion. Our growth hypothesis (Fig. 7) is based on ionic and atomic lithium diffusion and insertion and does not include the macroscopic process of plastic deformation and flow [18].

In addition to this insertion of lithium into growing structures which are probably crystalline, [30] further details can be inferred from the observations. The structures at the tip (which we observed as extra features on some filaments in SEM images as the one shown in Fig. 8) which are not dissolved during anodization (Fig. 6) may be inoxidizable particles that participate in filament nucleation as suggested in Fig. 7a) and b), e.g. by changing the local SEI resistance, and in the propagation as proposed in Fig. 7c) and d). On the other hand, the inoxidizable particle can be a cap of SEI that forms during lithium deposition.

An ideal SEI would be completely homogeneous, causing homogeneous plating at its interface to the metal. However, an actual SEI will never be uniform and may include inorganic crystals of oxide, hydroxide, carbonate or fluoride or other components depending on the electrolyte composition [31]. Due to variations in the local conductivity or preferred aggregation of the discharged lithium atoms at irregularities in the SEI – drawn in red in

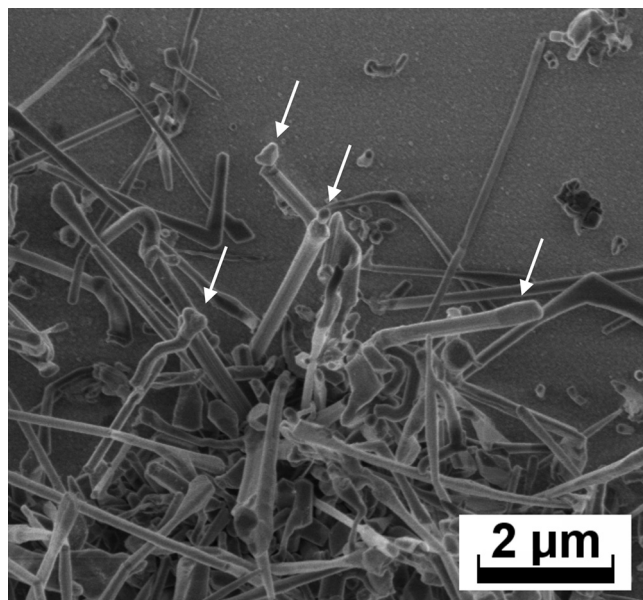


Fig. 8. SEM image (1 kV) of lithium filaments deposited on tungsten at -100 mV. Several filaments show structures at the tip e.g. contrast changes, contaminants such as particles or a broadening of the tip.

Fig. 7, the lithium metal structure can grow relatively fast at this localized defect, causing an instability with respect to uniform growth.

After nucleation, atoms can be added at defect locations, i.e. either the substrate/needle interface, at the top inorganic particle/lithium interface or at kinks along the needle. For this process, the permeability of the SEI is of importance. The freshly formed SEI which grows on the lithium filament has to be thin enough since a thick SEI would slow down metal deposition. If growth would be mainly controlled by the insertion at regions where the SEI is thin it would not be possible to explain the observed 1D growth, instead rounded shapes like Fig. S4 should result. In addition to SEI regions that are thin enough also crystalline defects are required. It may be assumed that the SEI is modified at defects, e.g. the growing SEI is quickly carried away with the growing metal so that the SEI remains thin at the insertion site.

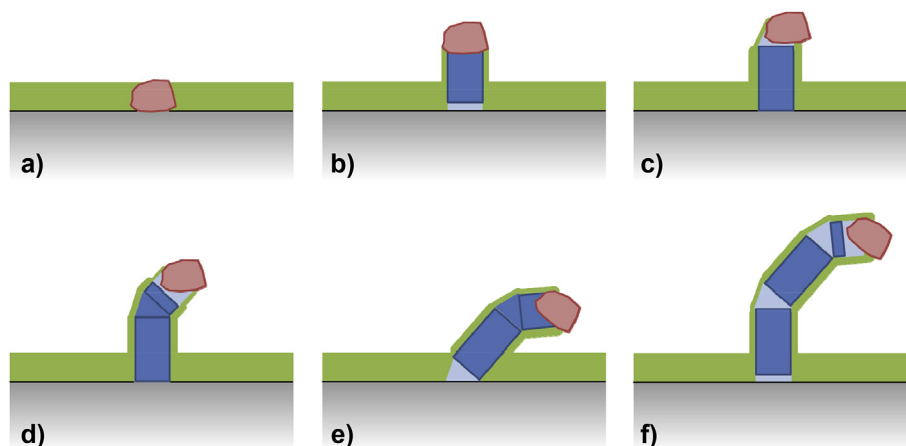


Fig. 7. Schematic describing growth of a lithium needle as observed in the *in situ* videos. The homogeneous components of the SEI – which are probably mainly organic – are drawn in green, Li insertion areas are light blue. The inoxidizable feature at the tip is depicted in red. a) initial state before lithium deposition with the inhomogeneity of the SEI shown in red, b) after growing a straight segment by lithium insertion at the substrate, c) after further deposition taking place below the tip, d) further deposition can result in a kink, e) additional Li was inserted at the base, causing tilting motions of the whole structure, f) final structure. All steps proceed by lithium insertion into the growing structure (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

Kinks can either form by a change in growth direction at the tip as suggested in Fig. 7c) and d), or at the base (Fig. 7d)–f)). We would like to emphasize that the growth zones of our model, placed in kinks or interfaces, easily explain the strong shaking and twisting motion that are present in the videos and that have been already observed by others [21,32]. In Ref. [21], the swinging behavior was explained by residual stress, but the large amplitude and angles involved would again require strong plastic deformation. In the interface or defect dominated growth presented here no stresses are needed to explain the motion of the growing structures. Instead, the motion is a consequence of non-uniform insertion at the base or at kinks.

Finally we emphasize that our observations have been performed with a particular liquid electrolyte (LP30, i.e. EC/DMC/LiPF₆) and a limited range of potentials and currents. For other cases, e.g. for higher currents or for polymer electrolytes with lower conductivity and lack of convection, the strong concentration gradient or even total depletion which are crucial for the models by Monroe and Newman [14] or Chazalviel et al. [9–11], respectively, can occur so that the corresponding models are applicable. The same is true for the other models: If there is growth at the tip, it will be faster due to spherical diffusion, but our observation of growth at the base suggests that this diffusion criterion alone is not sufficient to explain the strong tendency of lithium to form non-planar electrodeposits.

6. Conclusion

The growth and dissolution of electrodeposited lithium filaments have been observed. In addition to accretion at the tip region, unusual growth modes have been observed: growth in between kinks, but also growth from the base. Tip growth does not seem to occur at the outermost top, but behind an inactive structure. Based on the observations we suggest growth being dominated by insertion at crystalline defects, e.g. kinks or interfaces (Fig. 7). This should also apply similarly for so called bush-like or dendritic lithium. Several types of defects have to be considered: thin parts of the SEI causing enhanced deposition, defects in the crystal structure such as grain boundaries or maybe even amorphous regions, and chemical inhomogeneities such as contaminants that can cause alloy formation or may act as nucleation centers. For the conditions that we used during deposition, especially the liquid electrolyte, the observations are not compatible with previous explanations of lithium dendrite growth, e.g. with models that emphasize the field enhancement at tips, the strong influence of concentration gradients or the stress induced extrusion or motion.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2014.03.029>.

References

- [1] J.M. Tarascon, M. Armand, *Nature* 414 (2001) 359.
- [2] R. Jasinski, *High-energy Batteries*, Plenum Press, New York, 1967.
- [3] M. Matsui, *J. Power Sources* 196 (2011) 7048.
- [4] Z. Stachurski, United States Patent 3,440,098, 1969.
- [5] G. Clinckspoor, H. Schmidt, W. Vielstich, *Chem. Ing. Tech.* 42 (1970) 206.
- [6] Y.S. Cohen, Y. Cohen, D. Aurbach, *J. Phys. Chem. B* 104 (2000) 12282.
- [7] H.J.S. Sand, *Philos. Mag. Ser. 6* 1 (1901) 45.
- [8] A.R. Despić, K.I. Popov, in: B.E. Conway, J.O.M. Bockris (Eds.), *Modern Aspects of Electrochemistry No. 7*, Plenum Press, New York, 1972, pp. 199–313.
- [9] V. Fleury, J.-N. Chazalviel, M. Rosso, B. Sapoval, *J. Electroanal. Chem.* 290 (1990) 249.
- [10] J.N. Chazalviel, *Phys. Rev. A* 42 (1990) 7355.
- [11] C. Brissot, M. Rosso, J.N. Chazalviel, P. Baudry, S. Lascaud, *Electrochimica Acta* 43 (1998) 1569.
- [12] M. Rosso, T. Gobron, C. Brissot, J.N. Chazalviel, S. Lascaud, *J. Power Sources* 97–98 (2001) 804.
- [13] J.L. Barton, J.O.M. Bockris, *Proc. R. Soc. London, Ser. A. Math. Phys. Sci.* 268 (1962) 485.
- [14] C. Monroe, J. Newman, *J. Electrochem. Soc.* 150 (2003) A1377.
- [15] R. Akolkar, *J. Power Sources* 246 (2014) 84.
- [16] R.R. Chianelli, *J. Cryst. Growth* 34 (1976) 239.
- [17] F. Ding, W. Xu, G.L. Graff, J. Zhang, M.L. Sushko, X. Chen, Y. Shao, M.H. Engelhard, Z. Nie, J. Xiao, X. Liu, P.V. Sushko, J. Liu, J.-G. Zhang, *J. Am. Chem. Soc.* 135 (2013) 4450.
- [18] J.-i. Yamaki, S.-i. Tobishima, K. Hayashi, S. Keiichi, Y. Nemoto, M. Arakawa, *J. Power Sources* 74 (1998) 219.
- [19] T.A. Witten, L.M. Sander, *Phys. Rev. B* 27 (1983) 5686.
- [20] O. Crowther, A.C. West, *J. Electrochem. Soc.* 155 (2008) A806.
- [21] T. Nishida, K. Nishikawa, M. Rosso, Y. Fukunaka, *Electrochim. Acta* 100 (2013) 333.
- [22] F. Sagane, K.-i. Ikeda, K. Okita, H. Sano, H. Sakaebe, Y. Iriyama, *J. Power Sources* 233 (2013) 34.
- [23] A.M. Andersson, K. Edström, *J. Electrochem. Soc.* 148 (2001) A1100.
- [24] K.J. Harry, D.T. Hallinan, D.Y. Parkinson, A.A. MacDowell, N.P. Balsara, *Nat. Mater.* 13 (2014) 69.
- [25] K. Kanamura, S. Shiraishi, H. Tamura, Z.i. Takehara, *J. Electrochem. Soc.* 141 (1994) 2379.
- [26] G. Wranglén, *Electrochim. Acta* 2 (1960) 130.
- [27] M. Sobiech, M. Wohlschlogel, U. Welzel, E.J. Mittemeijer, W. Hugel, A. Seekamp, W. Liu, G.E. Ice, *Appl. Phys. Lett.* 94 (2009) 221901.
- [28] M. Sobiech, C. Krüger, U. Welzel, J.-Y. Wang, E.J. Mittemeijer, W. Hugel, *J. Mater. Res.* 26 (2011) 1482.
- [29] J.K. Stark, Y. Ding, P.A. Kohl, *J. Electrochem. Soc.* 160 (2013) D337.
- [30] X.H. Liu, L. Zhong, L.Q. Zhang, A. Kushima, S.X. Mao, J. Li, Z.Z. Ye, J.P. Sullivan, J.Y. Huang, *Appl. Phys. Lett.* 98 (2011) 183107.
- [31] P. Verma, P. Maire, P. Novák, *Electrochim. Acta* 55 (2010) 6332.
- [32] K. Nishikawa, T. Mori, T. Nishida, Y. Fukunaka, M. Rosso, T. Homma, *J. Electrochem. Soc.* 157 (2010) A1212.